



FT-Raman as a simple tool for the fast monitoring of reactions on silica-supported reagents and catalysts: application to silica-bound prolinol and TADDOLs

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Abstract—The application of simple NIR-FT-Raman techniques to the study of silica-supported reagents and catalysts is shown to be one of the more rapid and efficient methods for the characterisation of organic functional groups attached to silica surfaces and to monitor reactions occurring on them. Its use is illustrated in the study of novel routes for the preparation of silica-bound prolinol and TADDOL derivatives. © 2001 Elsevier Science Ltd. All rights reserved.

Over the past few years, intensive research has been devoted to the development of chiral heterogeneous catalysts.¹ The handling of immobilised catalysts presents many advantages, which are generally associated with a simplification of the work-up, the possibility of recycling and reusing them, the reduction of the environmental impact and the capacity of being used in continuous-flow systems or in automated syntheses.² Besides organic polymers, inorganic materials have been also used as supports.³ The immobilisation on an inorganic support can have some advantages. For instance, silica is rather chemically inert, can be used both at high or low temperatures and high pressures due to its superior mechanical and thermal stability, and has a structure with a highly accessible surface area. Some disadvantages are also present, as are the reduced number of functionalisation procedures and the low loadings that can be obtained. One of the most important drawbacks for the use of supported species is the limited range of analytical techniques available. Important achievements have been reported, in recent years, on the application of IR and NMR techniques to functionalised polymers,^{4,5} and an increasing number of applications are being described for the use of FT-IR and FT-Raman techniques (especially surface-enhanced Raman spectroscopy) to the study of adsorbed species on inorganic materials, in particular zeolites.^{4c} However, much effort is still required in this field for the development of new techniques for the characterisation

of the structures of the functional sites in those materials. Here we report how the use of simple NIR-FT-Raman spectroscopic techniques is probably one of the faster and easier ways to monitor reactions taking place on silica-supported organic species.

The heterogenisation of aminoalcohols and tartaric acid derivatives is attractive because of the easy accessibility of the starting materials and the variety of applications for those systems.^{3–10} Recently, we have studied the efficiency of some Ti- and Al-supported derivatives as Lewis acid catalysts for Diels–Alder reactions.⁷ In this context, we have observed how the nature of the organic support plays a crucial role on the outcome of the reaction.⁸ Accordingly, the preparation of the related silica-supported species is an interesting target.^{3,9,10}

The FT-Raman spectroscopy is a technique that gives structural information that is complementary to that obtained from FT-IR experiments. In general, it is considered that FT-IR is best suited for the characterisation of supported species as many organic functional groups are polar and give place to the appearance of strong absorption bands in the IR. It has to be taken into account, however, that some of those groups also show bands in the Raman, even if they are of lower intensity and that some groups are more active in Raman than in IR.^{11,12} For silica-derived materials, their physical properties and the low concentration of organic groups give place, very often, to the obtention of low quality FT-IR spectra. On the contrary, the nature of the NIR-FT-Raman techniques make them

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very appropriate for the analysis of silica surfaces, such as **2–8**, modified with organic groups.

The immobilisation of the chiral ligands was accomplished following the general route shown in Scheme 1.

Commercially available silica gel was derivatised with 3-mercaptopropyl groups to afford **2**.³ All attempts to obtain a good quality FT-IR spectrum of **2** were unsuccessful and even the presence of the S–H band could not be detected. However, a good quality NIR-FT-Raman spectrum of **2** (Fig. 1a) was obtained directly from the sample without any previous treatment, giving the desired structural information. It showed bands due to the methylene groups at 2910 cm^{-1} , and the presence of a band corresponding to the S–H bond at 2583 cm^{-1} . Additionally, bands corresponding to the C–S stretch and to the in-plane and out-of-plane C–S–H bending were observed at 649 , 916 and 480 cm^{-1} . As could be expected, no significant signals were obtained for the unfunctionalised silica **1**. A loading of 1.1 mmol g^{-1} of -SH was determined by combustion analysis.

The presence of the -SH group allowed the immobilisation of different chiral auxiliaries. In this sense, the vinyl derivative of prolinol **3** was attached to the inor-

ganic support **2** under radical conditions (AIBN) using CHCl_3 as the solvent to afford the silica-bound derivative **4**.³ After 12 h the silica was removed from the reaction vessel, washed, and dried under vacuum. The

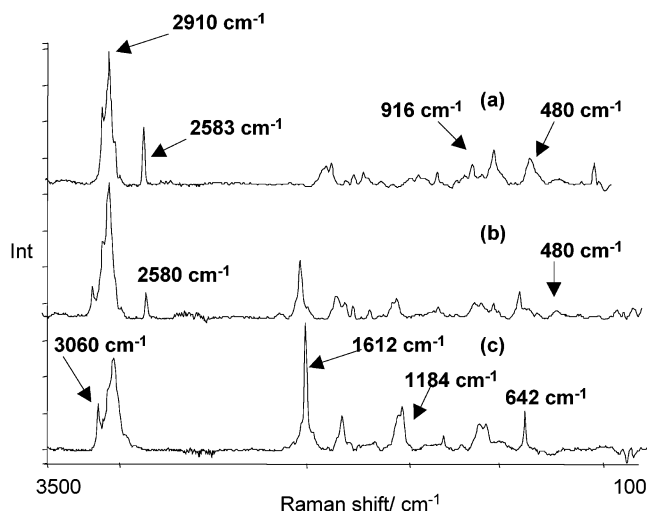
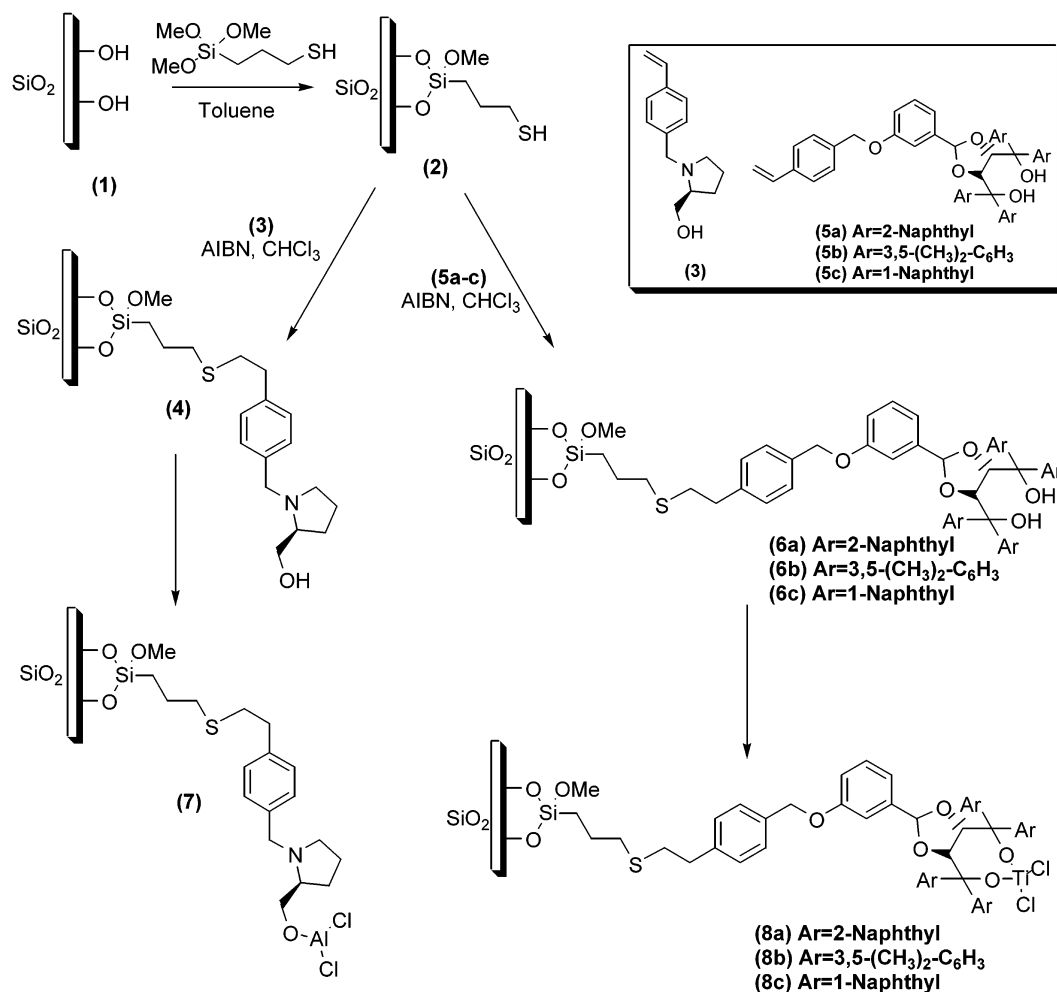


Figure 1. (a) NIR-FT-Raman spectrum of **2**. (b) NIR-FT-Raman spectrum after 24 h reaction of **2** with **3**. (c) NIR-FT-Raman spectrum after 48 h reaction of **2** with **3**.



Scheme 1. Synthetic procedures for the preparation of functionalised silica.

NIR-FT-Raman spectrum showed an incomplete conversion of the starting material **2** with a partial disappearance of the SH bands at 2583 and 480 cm^{-1} (Fig. 1b). When the reaction was carried out for 48 h, a complete disappearance of the SH bands was observed (Fig. 1c). Additionally, bands corresponding to different mode vibrations of the *N*-benzyl prolinol moiety were observed at ca. 3060, 1612, 1184 or 642 cm^{-1} .

The same methodology was used to carry out the immobilisation of different TADDOL derivatives containing styryl groups.^{7,8} Again the progress of the reaction could be easily monitored through the use of FT-Raman spectroscopy. As can be seen in Fig. 2a for **6a**, a complete disappearance of the SH bands was observed in all cases at the end of the reaction, confirming a complete transformation of the thiol groups. The resulting silica-bound compounds clearly showed also the bands characteristic for the functional groups introduced as is illustrated by the comparison of the Raman spectra for **6a** (Fig. 2a) and for its soluble precursor **5a** (Fig. 2b). The disappearance of the C=C band at 1628 cm^{-1} characteristic of the vinylic group in compounds **5** confirms that the anchoring reaction takes place according to Scheme 1.

Preliminary experiments for the study of those silica-bound derivatives as chiral auxiliaries in catalytic enantioselective processes were carried out by transformation of **4** and **6a–c** into the corresponding chiral complexes **7** and **8a–c** by treatment with EtAlCl_2 and $\text{Ti}(\text{OPr}^i)_2\text{Cl}_2$, respectively. Both kinds of complexes were checked as catalysts for the Diels–Alder reaction of cyclopentadiene and 3-crotonoyl-1,3-oxazolidin-2-one under similar conditions to those employed with related polymer-supported species.^{6–8} Initial results have shown some interesting trends. For instance, catalyst **7** showed a high activity (>90% yield after 3 h). This behaviour is similar to that found for the related

polymer-supported system and is in contrast with results observed for homogeneous analogues, for which the conversion was lower than 1% for the same period of time. As for polymer-bound systems, the inhibition of aggregate formation in the heterogeneous catalyst seems to be responsible for this behaviour.⁷ A reasonable *exo:endo* selectivity (4:1) was observed for **7**, but the enantioselectivity was very low (<5% ee). Silica-supported Ti-TADDOLates **8** displayed a lower activity than **7** (ca 40% yield after 3 h), an *endo:exo* selectivity of about 4 and again low enantioselectivities ($\leq 10\%$ ee). As with other supported catalysts the presence of additional functionalities can be at the origin of the low enantioselectivities observed. Most likely, improvement of these results would require a careful selection of the starting silica (silica gel 60, 0.06–0.2 mm for column chromatography was used for all the experiments), as well as a thorough control of the presence of other functional groups, in particular residual hydroxyl groups. Nevertheless, the possibility of using simple NIR-FT-Raman techniques for simple and fast analysis of the immobilisation of organic compounds on silica can greatly contribute to develop novel and more useful materials of this class.

Acknowledgements

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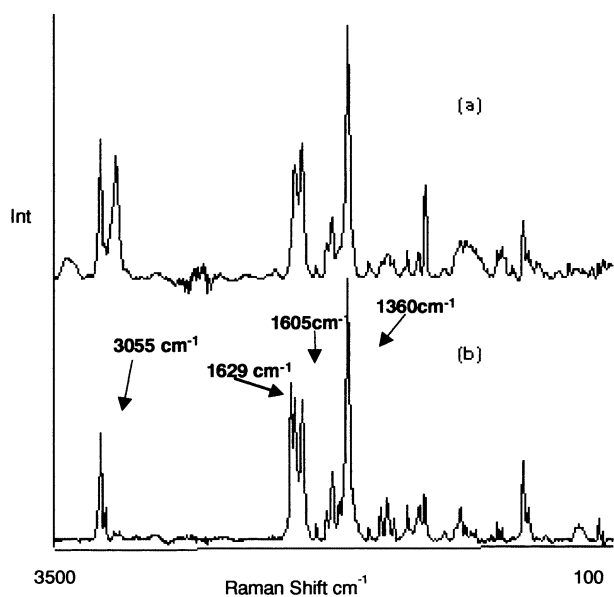


Figure 2. (a) NIR-FT-Raman spectrum of silica **6a**. (b) NIR-FT-Raman spectrum of the monomer **5a**.

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 - NIR-FT-Raman spectra were obtained using FT-IR and NIR-FT-Raman Perkin–Elmer Spectrum 2000 instrument equipped with a diode-pumped Nd:YAG laser PSU and using standard Spectrum v2.0 software. Samples of the functionalised silica were analysed with no previous treatment using standard Raman holders. The localisation of the sample was manually adjusted, for each case, in order to obtain the maximum intensity for a laser power of 710 mW. In all cases the resolution was adjusted to 0.1 cm⁻¹ and 100 scans were accumulated for each sample.